International Journal of Applied, Physical and
Bio-Chemistry Research (IJAPBCR)
ISSN(P): 2277-4793; ISSN(E): 2319-4448
Vol. 5, Issue 2, Oct 2015, 13-24

CONVERSION OF COAL FLY ASH TO A FRAMEWORK ALUMINOSILICATE UTILIZING ALKALINE HYDROTHERMAL SYNTHETIC METHODOLOGY

HEMA KUNDRA & MONIKA DATTA

Department of Chemistry, University of Delhi, Delhi, India

ABSTRACT

The amount of coal fly ash generated by coal-based thermal power plants has been increasing at an alarming rate throughout the world. Low amount of beneficial nutrients, low cation exchange capacity, high alkalinity are some of the factors responsible for its limited utility. In addition disposal of such a huge quantity of fly ash requires about 50,000 acre of a land with an annual expenditure of about Rs500 million for transportation. Several approaches have been made for proper utilization of fly ash, either to reduce the cost of disposal or to minimize the environmental impact. One of the approaches is the conversion of fly ash into zeolites, which have wide applications in ion exchange, as molecular sieves, catalysts and adsorbents. So the present study is aimed at the synthesis of zeolite from coal fly ash using hydrothermal synthetic methodology. The mechanism of zeolite crystallization and role of alkali solution the synthesis reaction is also discussed.

KEYWORDS: fly Ash, zeolite, hydroxysodalite, hydrothermal synthesis, reaction mechanism

INTRODUCTION

Electricity is a critical input needed for the development of any country and thermal power plant plays a pivotal role in fulfilling the growing energy demand **[01]**. Though there are different ways to generate electricity but the dominance of coal in the electricity production is likely to continue in foreseeable future since over 70 % of the electricity generated is from coal based power plants **[02, 03]** which generate more than 112 million tones of fly ash annually and it is projected to increase up-to 160 million tones per year. Because of the increase in the electricity generation, there is consistent increase in the requirement of coal leading to an increased production of fly ash **[02, 04]**. In addition, Indian coals have very high ash content (25 -45%) as a consequence, a huge amount of fly ash is generated in thermal power plants, so has become the largest amount of industrial waste in the world. As far as the disposal of fly ash is concerned, presently, the fly ash utilization for different purposes is less than 10% (of that is produced) in India, which is significantly less than that has been achieved in other countries, rest is disposed off as a waste causing yet another environmental concern **[05-07]**. Therefore; there is a need to encourage research on the development of materials using fly ash through novel synthetic methodologies.

High toxicity of fly ash with a remarkable persistence in the environment represents a potential danger for the health of ecosystems. Due to little amount of beneficial nutrients, high alkalinity, presence of hazardous leachable trace elements and low cation exchange capacity, it cannot be used as soil enhancer **[08]**. Major fly ash utilization area is the construction industry, which utilizes approximately 50% of the generated fly ash for several applications as admixture in cement/concrete, lime pozzolanic mixture (bricks/blocks etc.). The other usage of fly ash are low lying area fill (17%), roads and embankments (15%), dyke raising (4%), brick manufacturing (2%) and zeolite synthesis etc. **[09, 10]**. About 5-6% of total fly ash is used up in the above mentioned applications, and rest of it is disposed off in landfill sites and ash pools which is not only expensive but also causes serious environmental and health problems **[03, 11].** The annual

expenditure for the disposal of fly ash to ash dams is more than Rs. 500 million. Many attempts have been made for proper utilization of fly ash, either to reduce the cost of disposal or to minimize its impact on environment **[08]**. Therefore, recycling coal fly ash has important economic and environmental implications. Increasing concerns about the environmental consequences of such disposal have made us to put our efforts in the direction of cost effective process development for the conversion of fly ash to some value added product/s. The components of fly ash are some oxides derived from inorganic compounds, which remain after combustion of the coal. The main components of fly ash are SiO_2 and Al_2O_3, which are compositionally similar to natural zeolites **[12]**. Because of these similarities, more than 150 zeolites have been synthesized from coal fly ash **[4]**. Zeolites are microporous, hydrated aluminosilicates of alkali metals, alkaline earth metals, or other cations, which, in their crystal structure, contain numerous channels and chambers of different sizes (in A˚). High cation exchange capacity, high surface area and variable pore size are some of the special features which make them versatile materials for targeting wide range of applications e.g., materials for soil remediation and enhancement of plant growth, catalysts for chemical and petrochemical industries, adsorbents for a wide array of cationic and anionic pollutants, as ion-exchanger for nuclear wastes treatment etc. Other applications are in agriculture, animal husbandry and construction **[13]**. Therefore, cost effective production of zeolites using coal fly ash should constitute one important issue of waste management. Several research reports have been published on synthesis of zeolites **[14]** (P, A, X, Y, analcime, chabzite etc.) using various methods etc **[15-28]**. The best result reported so far, for the synthesis of zeolitic materials from fly ash using hydrothermal method, accounts for 50% (Berkgaut and Singer, 1995) , 45% (Hollman and Steenbruggen, 1998) and 40-55% (Querol et al, 2007) **[29-31].** In the backdrop of above information, it is apparent that the fly ash, if managed and utilized properly can be a beneficial raw material for possible use in different areas. Hence, an attempt has been made in developing a cost effective hydrothermal synthetic procedure for conversion of fly ash in to a highly crystalline single product aluminosilicate (zeolite) with high surface area and cation exchange capacity.

EXPERIMENTAL

Materials

In the present investigation, fly ash sample was procured from National thermal Power Plant, India and sodium hydroxide(AR,98%) Pure was procured from Qualigens, India. The aluminosilicate from fly ash was synthesized by the modification of the reported procedure **[18].**

Synthesis

In order to convert fly ash into a value added product, the complete dissolution of the fly ash, in the form of a gel, has been done by heating the alkali and fly ash mixture. After the formation of the gel, the solution was kept for ageing step (close to the room temperature) followed by the curing /crystallization step as per the reported literature. 5g of fly ash sample was taken; fly ash sample was sieved to eliminate larger particles. The fly ash was added to sodium hydroxide solution in a conical flask to make the slurry and was stirred at various temperatures followed by ageing and curing. The resultant mixture was then cooled to room temperature and then washed several times with double distilled water to eliminate extra alkali followed by drying in oven at 60-70°C for 6-7 hours.

Characterization

Various analytical techniques have been employed for this purpose. To identify crystalline materials in the

samples, X-ray diffractograms were recorded on Philips PW3710 X-ray Diffractometer using Cu Kα (alpha) radiations with tube voltage 45 kV and 40 mA with a sampling step of 0.02° and a scan time of 4sec in 2θvalues ranging from 10-70°. Infrared spectroscopic (FT-IR) studies were carried out to identify their structural features. FTIR spectra were taken in KBr on a Perkin Elmer FTIR spectrophotometer. For each sample, spectrum has been recorded for 64 scans with 4cm^{-1} resolution between 4000–400cm^{-1} . To avoid the interference from the CO_2 and water, IR chamber was flushed with dry nitrogen. Morphology of fly ash and synthesized product were investigated by using scanning electron microscopic studies (SEM), the SEM analysis has been performed on ZEISS EVO Scanning Electron Microscope Model EVO 50. Thermal stability was investigated by thermo gravimetric (TGA) methods. TGA was recorded on Shimadazu DTG 60 at a heating rate of 30°C/min upto 700°C and a flow rate of 100mL/min. EGME method was used to determine the Specific surface area and ammonium acetate method was employed to determine Cation Exchange Capacity (CEC). Solid state NMR spectra was obtained using INOVA 400 Solid State NMR spectrometer.

RESULTS AND DISCUSSIONS

X-Ray Diffraction Studies

The X-ray powder diffraction patterns of fly ash and the synthesized product S-01and S-02 (“Figure 1” a and b) indicates the total conversion of fly ash to a highly crystalline aluminosilicate. A relatively broad band centered at 2θ = 26.2° is the characteristic feature of class F fly ash (glassy phase) having relatively low calcium content (figure 1a) **[32, 33]**. The presence of sharp peaks at 2θ = 16.34 (5.41), 30.81 (2.89), 33.11 (2.70), 35.12 (2.55), 39.13 (2.29), 40.73 (2.21), 60.50 (1.52) and at 2θ = 20.77 (4.27), 36.79 (2.44), 49.99 (1.82), indicates the presence of predominantly mullite ($3Al_2O_3.2SiO_2$) and quartz (SiO_2) respectively, as the crystalline material (JCPDS no. 15-0776 and 05-0490). The halo pattern in the background between 2θ = 10.2° and 2θ = 40.2° indicates the presence of amorphous material **[34].** Appearance of crystalline phase/material and the absence of the representative peaks of the fly ash (Figure 1” b) in the synthesized product(S-02) are indicative of conversion of fly ash in to a highly crystalline aluminosilicate **[35, 36]**. Presence of peaks corresponding to quartz and mullite is usually reported to be present, during hydrothermal process, along with the final product **[37-40]**.The diffraction intensities of the synthesized product(“Table 1” and “Figure 1” b) were identified with the help of JCPDS (Joint Committee on Powder Diffraction Standards for inorganic compounds) – No. 11-0401 files and “h, k, l”, “a, b, c” and α, β, γ values have also been calculated using “Powder-X” software.

Table 1: XRD Data for Sample No. S-02

2θ in Degree	D-Value in Å	
	Observed	Reported
13.91	6.36	6.28
19.69	4.50	4.44
24.24	3.66	3.63
31.46	2.84	2.81
34.56	2.59	2.56
37.45	2.39	2.37
42.69	2.11	2.09
47.50	1.91	1.98
49.75	1.83	1.81
51.93	1.75	1.73
58.12	1.58	1.57
60.07	1.54	1.52

Crystallographic Data Calculated from "Powder-x" Software:

Symmetry: Cubic

Cell Parameter: $a = b = c = 8.9746Å$

Cell Volume: $722.854\ Å^3$

$\alpha = \beta = \gamma = 90$

The calculated values from powder-X software suggest that the cubic structure for the synthesized product is in good agreement with hydroxysodalite structure **[35, 36, 41-43]**.

(a) (b)

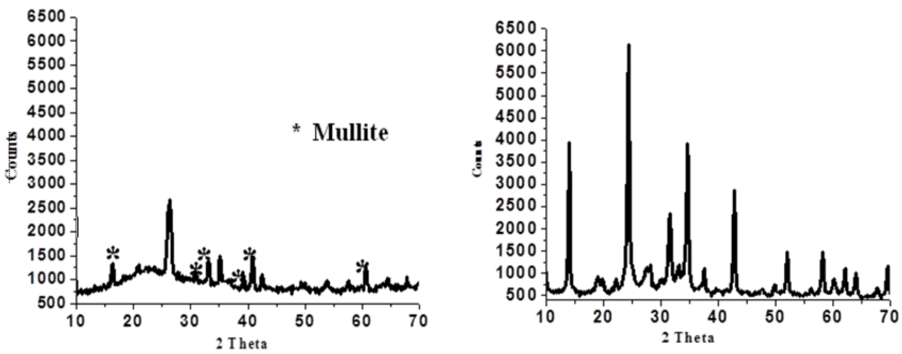


Figure 1: XRD Patterns of Fly Ash (a) and the Product (b)

Fourier Transformed Infrared Spectroscopic Studies

The FTIR spectra ("Figure 2" a and b) of fly ash (S-01) and the synthesized product (S-02) indicate the conversion of fly ash to crystalline aluminosilicates. The presence of quartz and mullite as evident from the presence of peak at 1096 cm^{-1} and 470 cm^{-1} ("Table 2") **[44]**.

Table 2 Vibrational Frequencies of Fly Ash

Vibrational Frequencies (cm^{-1})		Assignments
Observed Values	Reported Values	
1096(s), 906(sh)	1135-1080	Si/Al-O, Asym. Sretching Quartz & Mullite
Broad Shoulder	792-700	Si/Al-O, Sym. Sretching Quartz & Mullite
560 (s), 458(s)	560-550, 460	Si/Al-O, Bending Mullite, Quartz

Absence of representative peaks of fly ash ("Figure 2" a and "Table 2") **[40]**, in the FT-IR spectra of the synthesized product, S-02 ("Figure 2" b and "Table 3") suggests the total conversion of fly ash into crystalline aluminosilicate. The observed infra red vibrational bands of the synthesized product, S-02 has been assigned with the help of the available reported values for similar compounds ("Table 3") **[43, 45-49].** The 1200-950 cm^{-1} region mainly represents the strongest vibrational bands originating from the asymmetric stretching vibrations of Si-O-Si and Si-O-Al

linkages. Vibrational frequencies of these bands have been observed to decrease with increasing number of Al^{3+} in the framework **[49-51]**. This band is observed at 1096 cm^{-1} in fly ash (originating from quartz and mullite) and shift, to a lower frequency of 989 cm^{-1} in case of the synthesized product, suggesting the incorporation of more Al^{3+} ions and the formation of a framework structure. Observed frequencies suggest that the structure for the synthesized product is in good agreement with the reported values for the hydroxysodalite structure (“Table 3”) **[43]**.

Table 3: Vibrational Frequencies of the Synthesized Product, S-02

Vibrational Frequencies (Cm^{-1})		Assignments
Product S-02	Reported Values for Similar Compounds	
3518(s)	3440-3520(s)	O-H stretching Zeolitic Water
1663(ms)	1635-1660(ms)	O-H bending region Zeolitic Water
989 (s)#	986(s)	Si/Al-O, Asym. Stretching
718(w), 696(mw), 658(ms)##	729(m), 701(mw), 660(ms)	Si/Al-O, Sym. Stretching
463 (ms), 434 (ms)###	461 (ms), 432 (ms)	Si/Al-O, Bending

 # -Ref. No. 45-47
 # # - Ref. No. 43
 # # # - Ref. No.43, 48-50

(a) **(b)**

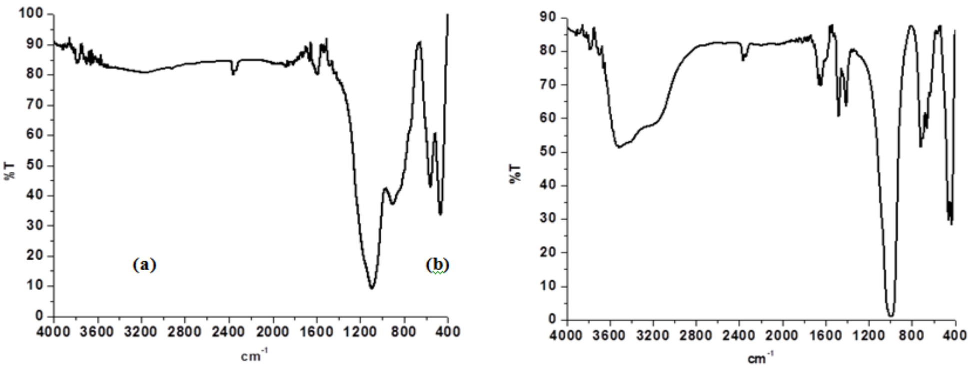


Figure 2: FT-IR Spectra of Fly Ash (a) And the Product (b)

Scanning Electron Microscopic Studies with EDX Analysis

The SEM picture of the fly ash (“Figure 3” aand b) indicates smooth spherical surface **[33]** with particle size ranging from 2 to 5 μm. Decrease in particle size and well defined cubic crystals indicate the complete transformations of fly ash as has been confirmed by the XRD data and EDX data **[52]**. Elemental analysis was obtained from SEM-EDX studies (“Table 4” a and b). Synthesized product with 1:1 Si: Al ratio with hydrated Na in the cages (α and/or ß) with trace amount of other impurities.

Table 4a: EDX Data of Fly Ash

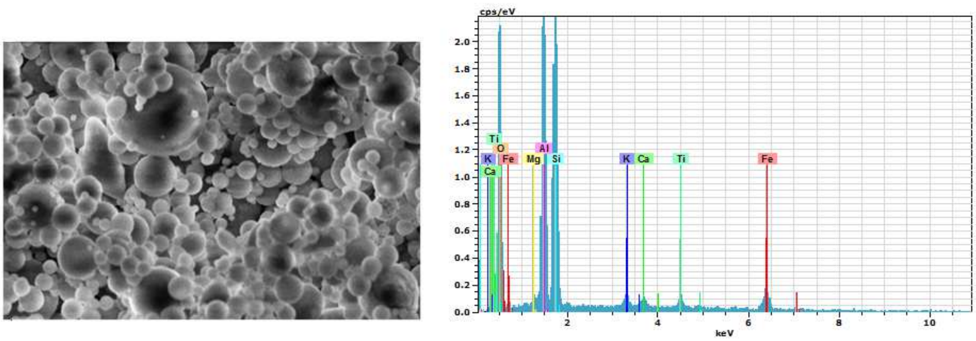
Element	Spectra. Type	Element %	Atomic %
O K	ED	56.56	70.32
Na K	ED	00.06	0 0.05
Al K	ED	16.41	12.10
Si K	ED	21.71	15.37
K K	ED	00.81	0.41
Ca K	ED	00.70	0.35

Ti K	ED	01.13	0.47
Fe K	ED	02.63	0.94
Total		**100.00**	**100.00**

Table 4b: EDX Data of S-02

Element	Spectra Type	Element %	Atomic %
C K	ED	18.22	25.73
O K	ED	53.00	56.19
Na K	ED	9.26	6.83
Al K	ED	8.15	5.13
Si K	ED	8.77	5.30
Ti K	ED	0.63	0.22
Fe K	ED	1.96	0.60
Total		100.00	100.00

(a)



(b)

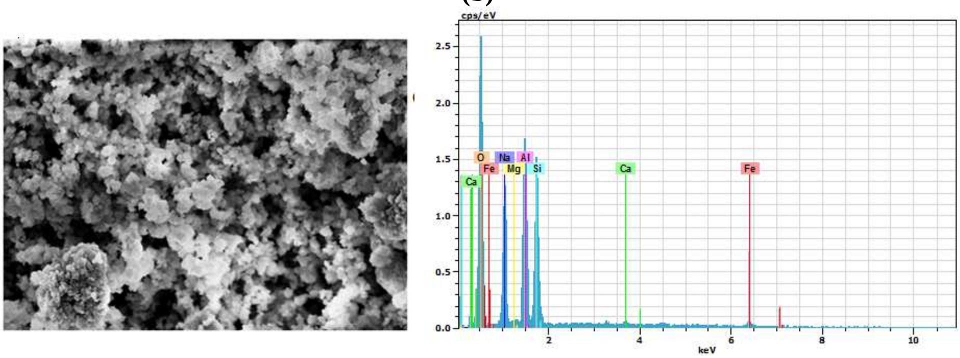


Figure 3: SEM Picture and EDX Data of Fly Ash (a) And the Product (b)

Thermogravimetric Studies

In case of fly ash (“Figure 4”a) first weight loss of 0.2% is observed in the temperature range of 35-200°C

(corresponding to the loss of physically adsorbed water) followed by a weight loss of 1.8% in the temperature range of 200-550°C (attributed to the decomposition of hydrated salts such as Ca $(OH)_2$. xH_2O, $CaSO_3.xH_2O$, etc. present in fly ash). In the temperature range of 550-700°C 0.8% weight loss (attributed to the loss due to the oxidation of unburnt carbon and decomposition of metal carbonates in fly ash) has been observed **[53, 54]**. Two step weight losses in case of S-02 have been observed. The first step (30°C to 100°C) amounts to a loss of 3.2%, corresponds to the loss of physically adsorbed water. The second step (100°C to 250°C), amounts to a loss of 4.6% corresponds to the loss of metal bound water and water located in zeolitic cavity ("Figure 4b) **[55]**. The total percentage of weight loss in case of fly ash has been relatively very small (2.8%) due to non-framework structure. The presence of cavities and voids in the framework is responsible for the retention of relatively large amount of water.

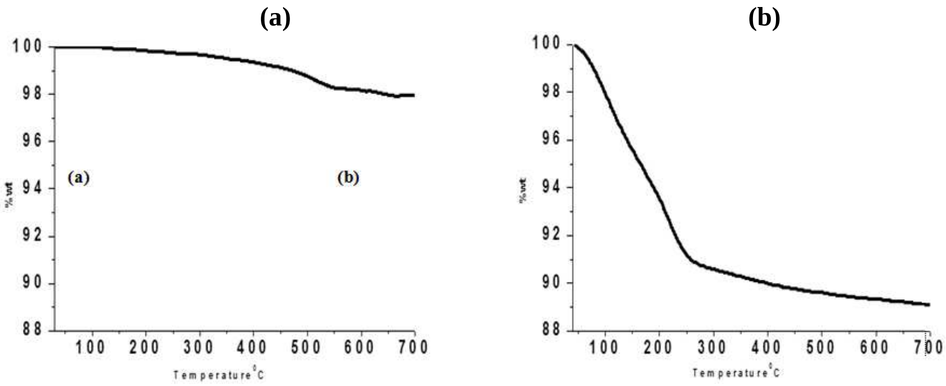
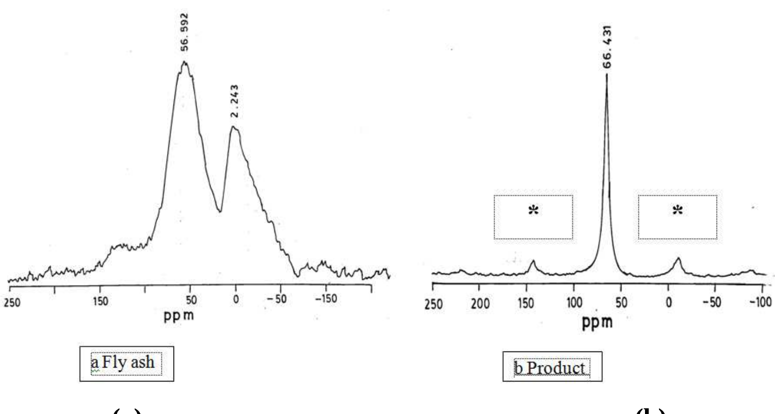


Figure 4: Thermograms (TGA) of Fly Ash (A) And the Product (B)

Mas-Nmr Spectroscopic Studies

Al^{27} mas-nmr spectroscopic studies

The Al^{27} NMR spectra of fly ash ("Figure 5" a) indicates two types of coordination of Al with oxygen, the resonance at 2.243 ppm and at 56 ppm corresponds to the octahedrally and tetrahedrally coordinated Al atoms respectively **[50, 51, 56]**. In case of the synthesized product ("Figure 5" b) a sharp and intense resonance at 66.43ppm corresponding to the tetrahedrally coordinated Al atoms and two side spinning bands at -12ppm and 142ppm, originating from the quadrupolar interactions of Al^{27} species confirms the presence of Al in the product **[52].**



(a) (b)
Figure 5: Al^{27} MAS-NMR of Fly Ash (A) and the Product (B)

Si^{29} mas nmr spectroscopic studies

The Si^{29} NMR spectra of fly ash ("Figure 6" a) indicates two types of coordination of Si with oxygen, the resonance at 105.678 ppm and at -88 ppm corresponds to the octahedrally and tetrahedrally coordinated Si in mullite and quartz respectively **[56, 57]**.In case of the synthesized product, a sharp and intense resonance at -84.785 ppm has been observed corresponding to the tetrahedrally coordinated Si atoms ("Figure 6" b).It is also an indication of the presence of Si-O-Al linkages i.e.[Si (2Si, 2Al)] **[18]**. The presence of a single resonance indicates cubic symmetry and confirms the alternating Si, Al order with identical Si-O-Al bond angles of sodalite framework (i.e. Si/Al =1) **[58, 59]**.

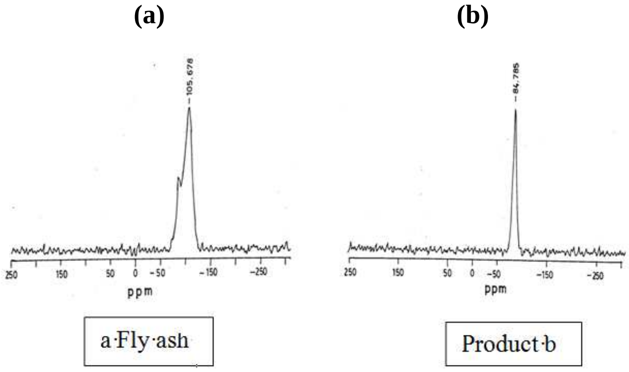


Figure 6: Si^{29} MAS-NMR of Fly ash (a) and the Product (b)

Total Surface Area and Cation Exchange Capacity Studies

Total surface area was estimated by EGME method and was found to be 133m^2/g and 422 m^2/g for fly ash and the synthesized product respectively. An increase in surface area is due to the porous structure of the frame work and is also evident from the scanning electron micrographs **[60]**.Cation exchange capacity of fly ash and the product was estimated by using the sodium acetate method **[61, 62]** and it was found to increase from 5.73 meq/100g to 408.69meq/100g. The increase in CEC value also supports the presence of porous structure of the synthesized product.

Mechanism for Hydrothermal Synthesis of Zeolite

The major factors that help in the dissolution of coal fly ash in synthesis of zeolite are:

- Rise in temperature
- The OH^- ion in the alkali solution

As the temperature rises, the dissolution of fly ash as a first step and the particle surface changes from sphere to something like unevenness ("Figure 7"). The hydroxide (OH^-) act as an activator which helps in the dissolution of amorphous silica and alumina from fly ash to form soluble silicate and aluminates salts. In the next step, the condensation reaction of silicate and aluminate ions takes place, and they are condensed to form a gel (prematerial of zeolite crystal). As the condensation reaction proceeds, it begins to transform into a zeolite crystal as the crystallization step. Cations like Na^+

and K^+ present in alkali solution helps in the crystallization of zeolite **[16]**. So, the synthesis process of zeolites from fly ash consists of dissolution of metal oxides, gel formation, condensation of aluminate and silicate ions and crystallization from gel.

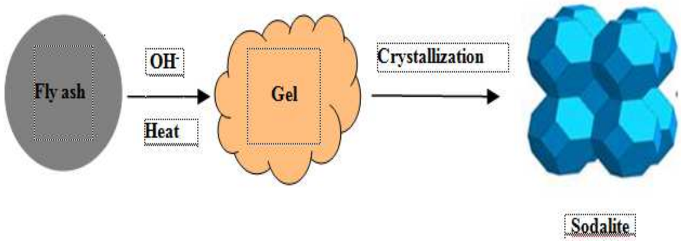


Figure 7: Proposed Mechanism for Hydrothermal Synthesis of Zeolite

CONCLUSIONS

From the characterization studies of fly ash and the alkali modified fly ash, it is concluded that complete conversion of fly ash to crystalline, single product (zeolite) with high surface area and cation exchange capacity has been achieved. The structure was found to have cubic hydroxysodalite type structure. Present process formulated here for the synthesis of zeolite from fly ash has the advantages of conservation of raw materials (sodium silicate and sodium aluminate), cost effectiveness, technically convenient, economical and non-tedious process, energy conservation, high value utilization and partially solving the fly ash disposal problem. So, the outcome of the proposed research work would lead to a cleaner and healthier environment

ACKNOWLEDGEMENTS

We express our sincere thanks to the following persons for providing instrumentation and other facilities to Department of Chemistry, University of Delhi, Dr. S. C. Datta, IARI, PUSA for extending XRD facility, AIIMS for extending the SEM facility, UGC for the financial support, NTPC for providing the fly ash samples, Dr. Shreedhar, IICT, Hyderabad for extending Solid State MAS NMR facility.

REFERENCES

1. U. Bhattacharjee et al (2002). Potential of fly ash utilisation in India. Journal of Cleaner Production, 27(2), 151-166.
2. S. R. Michalski et al (2001). Ash Disposal-Mine Fires-Environment: An Indian Dilemma. Bulletin of Engineering Geology and the Environment, 60, 23–29
3. Parisara, Envis Newsletter, Utility bonanza from dust, State Environment Related Issues (2007). 2(6), 1-8
4. U.Bhattacharjee et al (2002). Potential of Fly ash Utilization in India. Energy, 27, 151-166
5. R. S. Blissett et al (2012). A Review of the Multi-Component Utilization of Coal Fly Ash. Fuel, 97, 1–23.
6. M. Ahmaruzzaman et al (2010). A Review on the Utilization of Fly ash. Progress in Energy and Combustion Science, 36 (3), 327–363 **1**
7. P. Brown et al (2011). The Internal Microstructure and Fibrous Mineralogy of Fly ash from Coal-Burning Power Stations. Environmental Pollution, 159 (12), 3324–3333. **2**
8. S.Hernandez et al (2002). Zeolitic Material Synthesized from Fly ash: Use as Cationic Exchanger. Journal of Chemical Technology and Biotechnology,77,299-304

9. S.Rayalu et al (2000). Highly Crystalline Faujasitic Zeolites from Fly ash. Journal of Hazardous Materials B, 77, 123-131
10. Fly ash Utilization Programme (FAUP), Fly ash Management in India: An Intergrated Approach, Technology Information, Forecasting & Assessment Council, Department of Science & Technology, Government of India
11. H.A.Foner et al (1999). Characterization of Fly Ash from Israel with Reference to its Possible Utilization.Fuel, 78, 215-223
12. S.S.Rayalu et al (2006). Fly ash Based Zeolite Analogues:Versatile Materials for Energy and Environment Conservation. Catalysis Surveys from Asia,10(2),74-88
13. www.bza.org/zeoltes.html
14. L.R.G. Araújo et al (1999). Synthesis of Cubic Y Zeolite Using a Pulsed Microwave Heating System.Materials Research, 2 (2), 105-109
15. X.Querol et al (2002).Synthesis of Zeolites from Coal Fly ash:An Overview.International Journal of Coal Geology, 50, 413-423
16. N.Murayama et al (2002).Mechanism of Zeolite Synthesis from Coal Fly ash by Alkali Hydrothermal Reaction. International Journal of Mineral Processing, 64, 1-17
17. V.Berkgaut et al (1995). Cation Exchange Properties of Hydrothermally Treated Coal Fly ash. Environmental Science and Technology, 29, 1748-1753
18. H.L.Chang et al (1996). Conversion of Fly ash into Zeolites for Ion-Exchange Applications. Materials Letters, 28, 263-268
19. J.Chen et al (2006). Removal of Phosphate from Aqueous solution by Zeolite Synthesized from Fly ash. Journal of Colloid and Interface Science, 300, 491-497
20. S.Furusawa et al (2002). Synthesis,Characterization and Formation Process of Na-X Zeolite from Coal Fly ash. Journal of Materials Synthesis and Processing, 10(3), 143-148
21. K.S.Hui (2006). Effects of Step-Change of Synthesis Temperature on Synthesis of Zeolite 4A from Coal Fly ash. Microporous and Mesoporous Materials, 88, 145-151
22. M.Miyake (2002). Resource Recovery of Waste Incineration Fly ash:Synthesis of Zeolites A and P. Journal of American Ceramic Society,85 (7), 1873-1875
23. K.Ojha et al (2004). Zeolite from Fly ash: Synthesis and Characterization. Bulletin of Material Science, 27(6), 555-564
24. K.Petrus et al (2000). The use of a Modified Fly ash As an Adsorbent for Lead. Water SA, 26(4), 531-536
25. C.Poole et al (2004). A Comparative Study Using Two Methods to Produce Zeolites from Fly ash. Minerals Engineering, 17, 167-173
26. S.Sang et al (2006). Synthesis of Small Crystals Zeolite NaY. Materials Letters, 60, 1131-1133

27. V.S.Somerset et al (2005). Alkaline Hydrothermal Zeolites Synthesized from High SiO_2 and Al_2O_3 Co-disposal Fly ash Filtrates. Fuel, 84, 2324-2329

28. V.Somerset et al (2005). Alkaline Hydrothermal Conversion of Fly Ash Filtrates Into Zeolites 2: Utilization in Wastewater Treatment. Journal of Environmental Science and Health,40, 1627-1636

29. Arieh Singer et al (1995).Cation Exchange Properties of Hydrothermally Treated Coal Fly ash. Environmental Science and Technology, 29,1748-1753

30. G.Steenbruggen et al (1998). The Synthesis of Zeolites from Fly ash and The Properties of Zeolite Products. Journal of Geochemical Exploration,62,305-309

31. X.querol et al (2007). Synthesis of High Ion Exchange Zeolites from Coal Fly ash. Geologica Acta, 5(1),49-57

32. S.Diamond (1983). On the Glass Present in Low-Calcium and In High-Calcium Fly ashes. Cement and Concrete Research, 13 (4), 459-464

33. A.R.Brough et al (2001). Adiabatically Cured,Alkali-activated Cement-based Waste forms Containing High Levels of Fly ash Formation of zeolites and Al-substituted C-S-H. Cement and Concrete Research, 31, 1437-1447

34. F.Blanco et al (2005). Variation in Fly ash Properties with Milling and Acid Leaching. Fuel, 84,89-96

35. K.Katsuki et al (2007). Effect of Anion Species from Ca-sources on Framework Type of Na–Ca Zeolites Prepared at 80℃. Journal of Porous Materials, 14,401-407

36. M.Alkan et al (2005). The Effect of Alkali Concentration and Solid/Liquid Ratio on the Hydrothermal Synthesis of Zeolite Na-A from Natural Kaolinite. Microporous and Mesoporous Materials, 86,176-184

37. D.Wu et al (2008). Changes of Mineralogical–Chemical Composition, Cation Exchange Capacity and Phosphate Immobilization Capacity during the Hydrothermal Conversion Process of Coal Fly ash into Zeolite. Fuel, 87,2194-2200

38. C.Poole et al (2004). A Comparative Study Using Two Methods to Produce Zeolites from Fly ash. Minerals Engineering, 17,167-173

39. M.Inada et al (2005). Synthesis of Zeolite from Coal Fly ashes with Different Silica–alumina Composition. Fuel**,** 84, 299-304

40. M.Park et al (2000). Molten-salt Method for the Synthesis of Zeolitic Materials I. Zeolite Formation in Alkaline Molten-salt System, Microporous and Mesoporous Materials, 37,81-89

41. J.Felsche et al (1986). Crystal Structures of The Hydro-Sodalite $Na_6[AISiO_4]_6.8H_20$ and of the anhydrous sodalite $Na_6[AISiO_4]_6$. Zeolites**,** 6,367-37

42. M.M.J.Treacy and J.B.Higgins (2001). Collection of Simulated XRD Powder Patterns for Zeolites, Published on behalf of the Stucture Commision of the International Zeolite Association, IV Edition

43. D.W. Breck (1974). Zeolite Molecular Sieves: Structure, Chemistry and Use. John Willey & Sons, A Wiley Inter-science Publication

44. M.Criado et al (2007). Alkali Activation of Fly ash: Effect of The SiO_2/Na_2O Ratio Part I: FTIR study. Microporous

and Mesoporous Materials, 106, 180-191

45. Th.Perraki et al (2004). Mineralogical Study of Zeolites from Pentalofos Area,Thrace,Greece. Applied Clay Science, 25, 9-16
46. W.Mozgawa et al (2001). The Relation Between Structure and Vibrational Spectra of Natural Zeolites. Journal of Molecular Structure, 596, 129-137
47. H.Zhao et al (2004). Alteration of Kaolinite to Cancrinite and Sodalite by Simulated Hanford Tank Waste and its Impact on Cesium Retention. Clay and Clay Minerals, 52(1), 1-13
48. D.Zhao et al (1998). Characteristics of The Synthetic Heulandite-clinoptilolite Family of Zeolites. Microporous and Mesoporous Materials, 21,371-379
49. A. F. Jiménez et al (2005). Mid-infrared Spectroscopic Studies of Alkali-activated Fly ash Structure. Microporous and Mesoporous Materials, 86,207-214
50. P. A. Jacobs et al (1984). Structure and Reactivity of Modified Zeolites, 23-30
51. M. Park et al (2002). Conversion of Fly Ash to Swelling Mica:A New Approach for Recycling Fly Ash. Journal of Porous Materials, 9,291-298
52. P. Marturano et al (2000). Fe/ZSM-5 Prepared by Sublimation of $FeCl_3$:The Structure of the Fe Species as Determined by IR,^{27}Al MAS NMR and EXAFS Spectroscopy. Journal of Catalysis, 192,236-247
53. S. C. Burris et al (2005). Comparison of Heating Losses and Macro Thermogravimetric Analysis Procedures for Estimating Unburned Carbon in Combustion Residues. Energy & Fuels, 19, 1493-1502
54. H. Li et al (1997). Studies of Fly ash Using Thermal Analysis Techniques. Journal of Thermal Analysis, 49, 943-951
55. P. Castaldi et al (2005). Thermal and Spectroscopic Studies of Zeolites Exchanged with Metal Cations. Journal of Molecular Structure, 734, 99-105
56. M. Inada et al (2005). Microwave-Assisted Zeolite Synthesis from Coal Fly ash in Hydrothermal Process. Fuel, 84, 1482-1486
57. F. Skvara et al. Concrete based on fly ash geo-polymers. www.researchgate.net/publication/266568967, 185-197
58. G. Engelhardt et al (1989). ^{29}Si MAS N.M.R of Aluminosilicate Sodalites:Correlations between Chemical Shifts and Structure Parameters. Zeolites, 9, 182-186
59. G. Engelhardt (1993). Multinuclear Solid State NMR of Host-guest Systems with TO (T = Si, Al) Host-frameworks. A case study on sodalities. Analytical Chimica Acta, 283,967-985
60. L. Smart and Elaine Moore (2005). Solid State Chemistry : An Introduction. 3rd Edition
61. M. L. Jackson (1973). Soil Chemical Analysis, Publisher:Prentice HALL of India (Pvt.) Ltd., Indian Edition
62. D. Rungsuk et al (2006). "2nd Joint International Conference on "Sustainable Energy and Environment SEE-2006". 21-23 November